Edible shaped bodies, in particular flat and tubular films

The invention relates to edible shaped bodies based on plastifiable biopolymers, cleavage products or derivatives thereof and/or synthetic polymers made from natural monomers. They are mainly used as packaging films and sausage casings.

As edible sausage casings, there have proved useful, in addition to natural casings (for bockwurst especially sheep gut), only collagen films and tubes (DE-B 17 92 627 and US-A 3 535 125). Edible casings based on calcium alginate (DE-B 12 13 211) have not been able to establish themselves.

Edible collagen films and tubes are produced from cattle hides by a very complex and environmentally-polluting process. The hides are digested with acids (e.g. lactic acid) until the fibrils are obtained; the high-viscosity mass is extruded and precipitated and consolidated slowly and compactly using gaseous NH_3 or with NH_4OH. During drying, crosslinking (curing) then takes place, which strengthens the products to the extent that they withstand the scalding process without any significant loss of mechanical stability.

In contrast, it has not been possible to give the alginate-based sausage casings the necessary stability. In the case of these casings, owing to the action of the sausage emulsion and the brine, the poorly soluble calcium salt is gradually converted into the readily soluble sodium salt of alginic acid. The casings as a result lose their strength.

It was the object of the invention to provide edible shaped bodies, in particular flat and tubular films, which no longer have the abovedescribed disadvantages. In

addition, they are to be able to be produced from natural raw materials in a simple, inexpensive and environmentally friendly manner. For the use as sausage casings, in addition, the tubular films are to have the required functional properties. In addition to the mechanical, swelling and shrinkage properties, these include especially sufficient heat stability, scalding stability and hydrolysis stability. This means they must also be sufficiently resistant to the hot water or superheated steam used for the scalding.

The object is achieved by providing an edible shaped body in the form of a flat or tubular film based on plastifiable biopolymers or cleavage products or derivatives thereof and/or synthetic polymers of natural monomers which is produced by a process having the following stages:

a) mixing the biopolymers, cleavage products or derivatives thereof and/or the synthetic polymers with at least one edible plasticizer, at least one lubricant and at least one crosslinker,
b) melting the resultant mixture to give a thermoplastic mass,
c) extruding this mass and
d) calendering and/or stretching or blowing the product obtained from the extrusion to give the edible shaped body.

In a preferred embodiment, the biopolymers, the cleavage products thereof and/or the synthetic polymers are first mixed with the plasticizer and the lubricant and processed to form a thermoplastic mass. Not until then is this mass admixed with the crosslinker and extruded.

The edible shaped body can also have a different shape than that of a flat or tubular film. Instead of stage d), or in addition to this stage, if appropriate, other shaping processes then occur, such as injection molding

or thermoforming. An example of a shaped body produced in this manner is edible table utensils.

The process stages c) and d) need not follow one another directly. It is also possible to store the extruded mass in the interim, e.g. in the form of granules. If it is desirable or required for the respective application, the flat films or tubes of the invention can in addition be partly or completely heat-set.

Depending on the shape of the die (annular or slit-shaped), sheets or tubes form during the extrusion from the thermoplastic mixture, and can then be converted, by calendering and/or stretching in the longitudinal and/or transverse direction, or by blowing, into flat films or seamless tubular films. If required, the material is heated during the blowing, calendering or stretching (again). The edible flat or tubular films of the invention generally have a thickness or wall thickness of from 20 to 120 µm, preferably from 30 to 60 µm. In the case of the tubular films, the wall thickness generally increases with increasing internal diameter. By means of the stretching or blowing, the shaped body gains further mechanical strength.

The shaped body of the invention has the particular advantage that it may be produced in a particularly environmentally friendly manner without special precipitation and wash baths or any other sorts of baths. In the production process, the generally customary apparatuses for mixing and extrusion, in particular kneaders and single- or twin-screw extruders, can be used.

Preferred examples of the plastifiable biopolymers, of their likewise plastifiable cleavage products or derivatives and of plastifiable synthetic polymers are thermoplastic starch, starch derivatives (in particular starch esters, especially starch acetates and starch propionates; and in addition also starch ethers,

especially starch alkyl ethers), extrudable gelatins and other natural proteins, such as maize protein, wheat protein and rapeseed protein, casein and is derivates, chitin and chitosans, alginic acids and alginates, carrageenan (a galactose polysaccharide produced from seaweed), dextran, galactomannans (from carob bean meal, guar gum), pectins (polygalacturonic acids and methyl esters thereof) and polylactic acid (= polylactides). For the shaped bodies of the invention, there is thus a broad selection of starting materials of vegetable and animal origin available. Collagen is unsuitable. It is not available in consistent quality. The content of the biopolymers or cleavage products or derivatives thereof and/or of the synthetic polymers is generally from 10 to 90% by weight, preferably from 15 to 80% by weight, in each case based on the total weight of the shaped body.

Preferably, two or more of the starting materials are used together. They are expediently uniformly mixed and plastified at relatively high temperatures by relatively long kneading in a twin-screw extruder in the presence of a plasticizer, a plasticizing aid (= lubricant), a hardener (= crosslinker) and, if appropriate, a filler.

Suitable plasticizers are glycerol, diglycerol, sorbitol, sorbitol esters, triglycol, carboxymethylcellulose and other compounds which are suitable for food contact and are preferably already officially approved. The content of the plasticizer is generally from 0.5 to 50% by weight, preferably from 2 to 25% by weight, in each case based on the total weight of the shaped body.

Suitable plasticizing aids or lubricants are, especially, vegetable oils, in particular sunflower seed oil, rapeseed oil, olive oil and poppyseed oil. In addition, compounds suitable for use in foods, such as lecithins, triethyl acetylcitrate, sucrose esters, lactones (such as 12-hydroxystearic lactone), lactams and synthetic triglycerides. The content of lubricant(s) is generally from

2 to 30% by weight, preferably from 5 to 20% by weight, in each case based on the total weight of the shaped body.

Hardeners or crosslinkers which can be used are caramel (caramelized sugar, maillose), woodsmoke condensate, sugar aldehydes, dialdehydes (especially glyoxal and glutardialdehyde), dicarboxylic acids (particularly aliphatic dicarboxylic acids, such as oxalic acid, malonic acid, adipic acid and succinic acid), dicarboxylic anhydrides (partiuclarly adipic-acetic anhydride = diacetyl adipate), di- or triisocyanates (especially hexamethylene diisocyanate) and di- or triepoxides, polysaccharide aldehydes (particularly dialdehyde starch, dialdehyde alginic acid, dialdehyde pectic acid, dialdehyde gum tragacanth and dialdehyde gum arabic). Generally, suitable crosslinkers are those compounds which contain at least two reactive groups. The content of crosslinker(s) is generally from 0.2 to 30% by weight, preferably from 0.5 to 25% by weight, particularly preferably from 1 to 10% by weight, in each case based on the total weight of the shaped body.

For edible films, which are, for example, to be used for wrapping cooked ham, and are thus not exposed to high mechanical loading, crosslinkers of relatively weak action are sufficient, such as dicarboxylic acids, sugar aldehydes (mono- and disaccharides) or caramel. Sausage casings which are exposed to a higher mechanical load, especially during stuffing, and must also withstand the scalding process undamaged, in contrast, should be considerably more intensively crosslinked, which can be achieved particularly well by the use of a plurality of crosslinkers. For these, in addition, use may be made of dialdehydes, such as glyoxal or glutardialdehyde, di- or triisocyanates or di- or triepoxides.

To strengthen the shaped bodies of the invention, the mixture, if appropriate, can further comprise fibers,

preferably woodpulp fibers or cotton linters, and/or pigments, in particular inorganic pigments such as calcium carbonate.

Woodpulp fibers having a length of from 0.2 to 5 mm, preferably from 0.5 to 2 mm, are particularly suitable. The fiber content is expediently from 2 to 30% by weight, preferably from 5 to 20% by weight, in each case based on the total weight of the shaped body.

Although the short pulp fibers which act to strengthen are not digestible, as dietary fiber they do promote digestion. They are preferably disposed in a compact middle layer by using special dies, i.e. a layer of a fibrous polymer pulp is extruded into two fiber-free layers. It is also certainly possible to distribute the fibers over the entire cross-sectional area, i.e. to extrude only one fibrous polymer mixture. It is frequently advantageous to incorporate, in addition to the fibers, fillers, such as leather shavings.

As polymeric starting material, particular preference is given to mixtures of thermoplastic starch with an extrudable protein, particularly preferably gelatin. The ratio of starch to protein in this case is generally from 95:5 to 5:95. To improve stability to moisture and heat, in addition, chitosan or pectin can be added in an amount of from 3 to 30% by weight, preferably from 5 to 20% by weight, in each case based on the total weight of the polymer mixture. Mechnical stability can be increased still further if the thermoplastic starch is completely or partially replaced by starch acetate. By mixing in from 5 to 25% by weight, preferably from 8 to 22% by weight, of glycerol (in each case based on the total weight) and from 2 to 20% by weight, preferably from 5 to 15% by weight, of a natural oil, e.g. sunflower seed oil, the mixture is made soft and flowable, to simplify extrusion.

For hardening, in a preferred embodiment, from 0.8 to 5% by weight, preferably from 1 to 3% by weight, of caramel and, in addition, from 0.5 to 10% by weight, preferably from 1 to 5% by weight, of a dicarboxylic acid, such as oxalic acid, malonic acid or succinic acid, are mixed in.

For edible sausage casings it is expedient to add from 1 to 10% by weight, preferably from 2 to 6% by weight (based on total weight of all components) of a dialdehyde, such as glyoxal or glutardialdehyde, a diisocyanate, such as hexamethylene diisocyanate, a diketene, a diepoxide, a lactam or lactone (e.g. δ-gluconolactone). The mixture is melted and uniformly mixed by relatively long kneading at from 90 to 170°C, preferably at from 95 to 150°C. The melt can then either be immediately extruded or granulated for later processing.

The edible seamless tubes in a caliber range from 16 to 50, preferably from 18 to 30, are expediently produced by extruding through a ring die, followed by blowing. The area stretching ratio during blowing is generally from 1:5 to 1:20, preferably from 1:6 to 1:10, particularly preferably about 1:8.

The tubes can then, in a subsequent process step, be treated internally or internally and externally and thus further modified in their properties. In particular, post-hardening can be carried out here, either using ionizing radiation, e.g. with X-rays, or with the abovementioned hardeners and crosslinkers. These can then be applied in the form of solutions or dispersions. The tubes are then (as usual) dried in the inflated state between two pairs of squeeze rolls. This is followed by a generally known manufacturing step. Generally, the tubes are gathered in sections and the resultant shirred sticks are processed on conventional machines. The seamless tubular films are particularly suitable as sausage casings, in particular for small sausages. In

addition, the shaped bodies of the invention are also suitable for packaging other foods, e.g. cheese.

The broad base of natural starting polymers, additives and crosslinkers in addition makes possible a very broad variation of the properties expected of food casings, so that shaped bodies may be adapted precisely to highly specific requirements, as shown by the following examples. Percentages are percentages by weight, unless stated otherwise.

Example 1

a) Preparation of thermoplastic starch:
100 kg of potato starch were dried under reduced pressure to a water content of less than 0.3% and melted and well mixed with 50 kg of glycerol (99% pure) in a kneader at from 160 to 190°C; to abolish the helix structure of the starch, the melt was kept for 2 h at 170°C; the mass was then extruded and granulated. On subsequent storage of the granules, the starch remained in the amorphous state.

b) Blending and production of a film:

50 kg	of the granules under a) (33.3 kg of starch + 16.7 kg of glycerol) were admixed with:
25 kg	of extrudable gelatin,
10 kg	of woodpulp fibers,
2 kg	of sorbitol,
4 kg	of malonic acid,
8 kg	of sunflower seed oil and
1 kg	of caramel

The mixture was melted at 160°C in an extruder, uniformly dispersed and extruded through a 40 cm flat-film die, stretched (stretching ratio in the machine direction 1:4, in the transverse direction 1:10), cooled, conditioned to 8% moisture content and wound up. The properties of the

film produced in this manner are given in the table below:

Weight	Thick-ness	Ultimate tensile strength (dry) N/mm^2		Elongation at break in %		Swell-ing value
gm^2	µm	longi-tudinal	trans-verse	longi-tudinal	trans-verse	%
42	35	28	18	15	22	180

Meat products, in particular cooked ham, were wrapped with this film and covered with a net. After cooking, the net could be removed without problems. The cooked ham was then sliced together with the film casing. The film was oxygen- and smoke-permeable, but had low liquid- and fat-permeability.

Example 2

40 kg of partially acetylated starch having a degree of substitution of 2.2,
25 kg of extrudable gelatin,
5 kg of chitosan,
20 kg of glycerol,
3 kg of caramel,
2 kg of hexamethylene diisocyanate and
5 kg of sunflower seed oil

were thoroughly mixed. The mixture was melted at a temperature from 170 to 180°C, then kept at 175°C for 30 min and then extruded as a film through an 80 cm flat-film die, stretched, longitudinally 1:6, transversely 1:8), heat-set, conditioned (to a moisture content of 10%) and wound up. The properties of the film produced in this manner are given in the table below:

Weight	Thick-ness	Ultimate tensile strength (dry) N/mm^2		Elongation at break in %		Swell-ing value
gm^2	µm	longi-tudinal	trans-verse	longi-tudinal	trans-verse	%
48	40	35	24	12	26	168

The film is suitable for warpping the most varied types of meat products and can be consumed with them.

Example 3

a) Preparation of thermoplastic starch:
75 kg of potato starch were dried under reduced pressure to a water content of less than 0.3%, 25 kg of glycerol (99% pure) were added and the mixture was melted and mixed thoroughly in a twin-screw kneader at from 160 to 190°C. The melt was then kept at 175°C for 2 h, extruded and granulated.

b) Blending and production of a tube:

51 kg	of the granules under a) were admixed with:
20 kg	of extrudable gelatin,
10 kg	of chitosan,
10 kg	of sunflower seed oil,
5 kg	of malonic acid,
2 kg	of glyoxal and
2 kg	of caramel.

This mixture was melted at 175°C in an extruder, mixed thoroughly and extruded through an annular die having a diameter of 20 mm; between the die and the first guide roll, the tube was stretched by inflation longitudinally and transversely in a ratio of 1:8 (based on the area), cooled, laid flat and wound up.

In the water-soaked state, the tube had a bursting

pressure of 32 kPa and a static extension at 21 kPa of 23 mm. The wall thickness was 30 µm, and the weight was 40 g/m^2. The shirred sticks were stuffed with sausage emulsion on an automated stuffing machine, scalded, smoked and packaged.

Example 4

A mixture of

30 kg	of	extrudable gelatin,
20 kg	of	starch granules as under 3b),
20 kg	of	partially acetylated starch (®Sconacell S),
10 kg	of	glycerol,
10 kg	of	sunflower seed oil,
5 kg	of	glyoxal and
5 kg	of	caramel

was melted. A third of this melt was then mixed in a separate extruder with woodpulp fibers of a length of from 0.5 to 1.5 mm. Using a special die having a diameter of 18 mm, a three-layer tube was then produced by coextrusion, the inner and outer layers of which tube were fiber-free, while the central layer was fibrous. The tubular casing comprised 12% of fibers, based on the total weight.

Between die and tube roll, the tube was stretched by inflation, cooled, conditioned (10% by weight of moisture content), wound up and shirred. In the water-soaked state, the tube had a bursting pressure of 36 kPa, a static elongation at 21 kPa of 22 mm, a wall thickness of 32 µm and a weight of 38 g/m^2.

The shirred sticks were stuffed with sausage emulsion on automated stuffing machines, scalded and smoked.

Example 5

A melt was produced from

30 kg of extrudable gelatin,
20 kg of partially acetylated starch,
10 kg of pectin,
20 kg of glycerol,
10 kg of olive oil,
5 kg of glutaraldehyde and
5 kg of $CaCO_3$

and extruded as described in Example 3 to form a tube of caliber 20. It had the same properties as the tube described in Example 3.

Example 6

50 kg of potato stach (not dried) were kneaded with
10 kg of water and
10 kg of glycerol

at from 100 to 120°C for 2 hours. A substantial part of the water evaporated in the course of this. The resultant mass was mixed with 10 kg of glycerol and 1 kg of glyoxal and extruded at 140°C as described above through an annular die having a diameter of 20 mm and blown (area stretching ratio: 1:6). The properties of the film thus produced are given in the table below:

Weight	Thick-ness	Ultimate tensile strength (dry) N/mm^2		Elongation at break in %		Swell-ing value
gm^2	µm	longi-tudinal	trans-verse	longi-tudinal	trans-verse	%
38	40	32	24	15	20	120